Review Article: “Single Molecule Electrochemistry in Nanoscale Junctions”

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ABSTRACT

A number of techniques give the ability to tether single molecules between metallic electrodes and to measure their electrical properties. Such techniques can be deployed across a wide range of environments, but importantly for electrochemists they can be applied in electrolytes and with full electrochemical control of both contacting electrodes. This article discusses how such techniques have emerged as powerful tools for analyzing charge transport in single molecule junctions at electrode|electrolyte interfaces and gives outlooks for the future development of this field of single molecule electrochemistry in nanoscale junctions.

KEYWORDS: Single molecule electrochemistry, single molecule electronics, STM, scanning tunneling microscopy, electrochemical gating, electrolyte gating, electrochemical single molecule transistor.

1.0 Single Molecules

It could be considered that an ultimate limit in molecular electrochemistry has been achieved with the ability to electrochemically control single molecules. There are a variety of manifestations of such single molecule electrochemical studies,[1-5] but this review focuses on using a scanning tunneling microscope (STM) tip to “wire” molecules with appropriate anchoring groups at both ends between a conducting substrate and the STM tip.[4-5] In this configuration current flow through the molecular bridge can be monitored as the electrode potential of the substrate and STM tip are changed.[4] Since we have reviewed some aspects of the area of single molecule junction formation and characterization under electrochemical potential control recently,[6-7] this review has an emphasis on the latest results of interest as well as foundational studies.

2.0 Techniques

So, how can single molecules be “electrically wired”? There are various approaches to this, using an STM, mechanically formed break junction (MCBJ) or nano-lithographically created gaps. This review focuses on the STM methods, which can be broadly classified as either “non-contact” or “contact” approaches. In the former the STM tip is approached to the substrate electrode to very close distances, less than the molecular length, but avoiding metallic contact between tip and substrate

(Figure 1A).[4] At these close proximities molecule(s) can bridge between the tip and surface and this is apparent from the current-distance curves (inset, Figure 1) with current flow through the molecular junction as it is extended from B to D in this figure. This is called the "*I*(*s*)" or "*I*(*z*)" method, with *I* representing the current flow as the molecule is extended by distance *s* (or *z*) during the STM tip retraction. The other method is the STM break junction method (STM-BJ),[5] with the difference being that the STM tip contacts, or crashes, into the substrate and a metallic junction is then snapped in the STM tip retraction before the molecular junction forms in the freshly opened gap. Both methods reply on the collection of many hundreds or thousands of such junction stretching traces and statistical analysis of the data. Both methods are adaptable to measurements of single molecule electrical properties in a wide range of environments and importantly in the context of this review they can be applied in electrolyte solution and with electrochemical control. This means deploying an EC-STM with a four-electrode bipotentiostat configuration so that the tip and substrate electrode potentials can be independently controlled and also applying insulating coating to all but the end of the STM tip to minimize faradaic leakage currents.

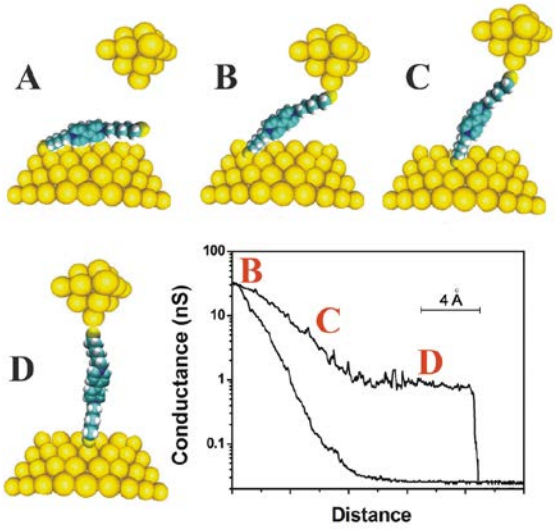

Figure 1. An illustration of the STM *I*(*s*) method for measuring current flow through single molecule junctions. The upper curve of the inset shows the junction conduction as a function of the stretching distance, while the lower trace shows exponential conductance decay for an empty junction. From Nichols et al., *Phys. Chem. Chem. Phys.*, 2010, **12**, 2801-2815 (ref. [8]) reproduced by permission of the PCCP owner societies.

While the great majority of studies of single molecule junctions in an electrochemical environment focus upon the possibility of 'gating' the conductance of redox-active molecules by controlling the overpotential, other motivations for carrying out such studies do exist. One example is the use of the so-called 'jump to contact' method. Here, a bipotentiostat is employed to electrodeposit a metal of interest onto an STM tip held outside tunneling distance, while leaving the second working electrode, the substrate, pristine. The tip is then brought to tunneling distance of the substrate, and

careful control of the potentials of the two electrodes is employed to transfer some of the metal of interest from tip to substrate. Retraction of the tip then enables measurement of single point contacts for the target metal, or alternatively in the presence of a suitable molecule it permits formation of metal/molecule/metal junctions, with the target metal as contact material. This has enabled the employment of metals that are less inert than the familiar gold or platinum, for example Cu, Fe or Pd.[9]

3.0 Redox Active Molecular Junctions

Using the electrochemical STM configurations and either the *I*(*s*) or STM-BJ methods a range of molecular redox systems has been studied. The *I*(*s*) technique was first applied to study the electrochemical redox switching of viologen molecular wires, which had thiol groups at each end to anchor them to the gold contacts.[4] As the electrode potential is made negative, the viologen (V^{2+}) is reduced to its radical cation ($V^{+\cdot}$) and this resulted in a pronounced increase in the single molecule conductance.[4] Here it can be viewed that the electrode potential "gates" the conductance of the molecular junction, with the conductance increasing as the potential is tuned to reduce the viologen. As such, this has been referred to as a "single molecule electrochemical transistor configuration" with the molecular bridge connected at either end by the thiol anchor groups to the gold source and drain electrodes and the reference/ counter electrode combination providing the electrochemical gating potential. The term "transistor" here refers to the control of the source-drain current flowing between STM tip and the substrate by the electrode potential or the electrolyte gating, in an analogous manner to a conventional field effect transistor. Viologens have been the most widely studied electrochemical single molecule junction system, with a focus on the electrochemical gating, charge transfer mechanisms and electrolyte effects.[4, 10-14] A number of other wired molecular bridges have been studied with electrochemical control including perylene tetracarboxylic acid (PTCDI),[15-18] functionalized benzodifuran,[19] pyrrolo-TTF (TTF = tetrathiafulvalene),[20-21] coronene,[22] oligo(phenylene ethynylene) derivatives (OPEs) with pendent nitro (-NO_2) groups, [23] anthraquinone molecular wires,[24-26] ferrocene-containing wires[27] and even DNA[28] and redox metalloproteins[29-31]. These studies have focused on a wide variety of properties of such electrochemically active single molecule junctions, including the influence of the electrode potential on charge transport across the bridge, achieving high off-on switching ratios, controlling quantum interference (QI) and contact and thermal effects (QI is a wave-like interference effect which can occur when electrons flow through molecules and can be seen as akin to other wave interference phenomena such as seen in the Young's double slit experiment with light).

Large on-off electrochemical switching ratios have been recorded for fully conjugated molecular bridges such as PTCDI.[15-18] 1,7-Pyrrolidine-substituted PCTDI derivatives are also noteworthy for exhibiting an "ambipolar" behavior, with gating at both negative and positive electrode potentials,[15] which has been related to electron- and hole-dominated transport, respectively. The choice of anchoring group has also been shown to be influential, with electrochemically-gated on/off switching ratios of benzodifuran-containing redox active junctions being enhanced with carbodithioate–

anchored molecular wires as compared to the more conventional thiol-contacted ones.[19] Electrochemistry has also been used to achieve direct anchoring of molecular wires through Au-C bonds. In this case, diazonium-terminated molecular wires have been reduced in situ in the electrochemical STM to achieve the Au-C anchoring at both ends of the molecule to the gold STM tip and substrate, respectively.[32]

Although not an experiment involving true electrochemical control, the presence of an electrical double layer has been invoked to rationalize the observation of large rectification ratios in STM-BJ experiments on gold/molecule/gold junctions using thioether-contacted, highly electron-deficient oligo(thiophene-*S,S*-dioxide)s.[33] The conductances of these junctions were significantly higher when the STM tip was biased negative with respect to the substrate than for the same magnitude positive bias when the experiments were conducted with wax-insulated tips in propylene carbonate (PC), but not when using nonpolar 1,2,4-trichlorobenzene as the medium. The rationalization for this observation is that adventitious ions in PC create a double layer, and the much smaller area of the coated tip means that the double layer is much more intense at the tip, so the LUMO-based molecular resonance is pinned to the tip potential, and as the latter is made more negative, a larger proportion of the transport resonance falls within the bias window. This technique has recently been adapted to provide a straightforward method to determine whether the conductance of a molecule is HOMO- or LUMO-dominated.[34]

The electrical properties of double-stranded DNA have been a subject of intense and interdisciplinary interest for some time.[35] The importance of π-stacking of bases in determining the double helical ds-DNA structure, and the role of π -stacking in determining the electrical properties of films of π -conjugated organic semiconductors in organic electronic devices,[36] indicates the likely importance of hopping in ds-DNA conductance, and recent results from STM-BJ measurements bear this out. Recently, a π-stacked anthraquinone redox moiety was incorporated into a short guanine:cytosine (G:C) sequence ds-DNA molecule bearing terminating alkanethiol units for binding to gold.[37] The STM-BJ method was used to investigate the conductance of junctions incorporating this molecule as a function of redox potential. Unlike other single molecule studies of this kind, where the conductance changes as a function of potential, in this instance two distinct conductance values ($3.7\pm0.5 \times 10^{-4}G_0$ for the oxidized form and $30\pm3 \times 10^{-4}G_0$ for the reduced form) were observed, and only the proportions of these forms changed as a function of potential.

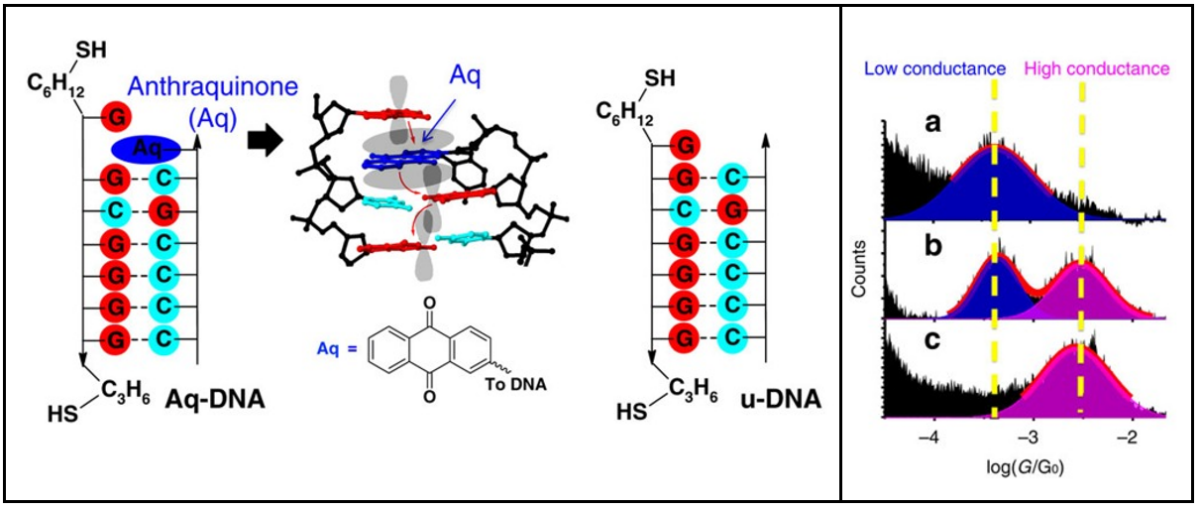

Figure 2. (Left Panel) Schematic of incorporation of anthraquinone into oligo-GC dsDNA. (Right) Conductance histograms of anthraquinone-functionalized dsDNA as a function of redox potential, showing progressive switching of oxidized form (blue peak in histograms) to reduced form with higher conductance (purple peak in histograms) as a function of more negative potentials. Reproduced from Xiang et al., reference [37], Nature Publishing Group.

Transition metal complexes afford good opportunities for incorporation into redox-active molecular wires, and in addition, they can confer other potentially useful properties such as paramagnetism (for possible spintronic applications). The strictly linear, metal-metal-bonded oligomers supported by oligo(amidopyridine)-type ligands, known as Extended Metal Atom Chains [38] (EMACs,) have previously been incorporated into gold/molecule/gold junctions by replacing the labile terminal halide ligands with thiocyanate (M-NCS) to give contacts, and electrochemically, many of these exhibit several reversible redox processes (see ref. [39] for chemical structure). In an early STM-BJ study, a correlation between conductance and mean metal-metal bond order was found for EMACS with a chain of 5 metal atoms (M) with M = Ni(II) ($5.4 \times 10^{-4} G_0$), Co ($1.3 \times 10^{-3} G_0$) and Cr ($4.1 \times 10^{-3} G_0$); bond orders 0, 0.5 and 1.5, respectively.[39]

More recently, re-examination of the conductance of these molecules as a function of electrochemical potential gave similar conductance values for the neutral forms, but on one-electron oxidation, the conductance of the Ni complex increased by 40%, whereas the Co complex conductance was unaffected.[40] The conductance histogram of the Cr complex showed two distinct values ($48.8 \pm 1.0 \times 10^{-4} G_0$ and $9.5 \pm 1.2 \times 10^{-4} G_0$) for the neutral form, but only one value ($10.8 \pm 1.3 \times 10^{-4} G_0$) for the mono-cation. The neutral form has been shown by careful X-Ray crystallographic and spectroscopic studies to consist of two bond length isomers, one in which Cr≡Cr bonds alternate with non-bonded pairs of Cr ions, the other in which the bonds are fully delocalized and of order 1.5, and it is suggested that it is the latter that is responsible for the high conductance value. The mono-cation, however, does not have two such isomers, existing in the localized state only. This paper also introduces a useful variation on the electrochemical STM-BJ technique. The

potentials of the two working electrodes (tip and substrate) are simultaneously scanned while a molecular bridge is present, allowing the peak which is usually observed in conductance-potential relationships to be determined for a given redox process without the need to collect steady-state STM-BJ data at a substantial number of (fixed) electrochemical potentials, which is a very time-consuming process. An interesting feature of these experiments is that the conductance appears to fluctuate in the region of this peak. An added refinement was the collection of Fowler-Nordheim (FN) plots (in which $\ln(I/V^2)$ is plotted against V^{-1}, where V is the bias voltage and *I* the current) are under electrochemical potential control; interestingly, the transition voltages observed in the FN plots reached a minimum at the redox process $E_{1/2}$.

4.0 Beyond Aqueous Electrolytes

There are good reasons for moving beyond the aqueous electrolytes which have featured in the vast majority of electrochemical single molecule studies. The most compelling reason is an ability to address redox states that are not accessible in aqueous electrolytes. The choice then is organic electrolytes or ionic liquids. The latter have been shown to be particularly rewarding for single molecule electrolyte gating and also for single molecule electrochemical scanning tunneling spectroscopy. [10, 20, 41-42] In aqueous electrolytes only the first oxidation of pyrrolo-TTF molecular wires could be reached.[21] However, using the room-temperature ionic liquid (RTIL) 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIOTf) three redox states of pyrrolo-TTF could be addressed (see Figure 3 for single molecule conductance versus electrode potential through all 3 redox states of this system).[20] Two-step electrochemically assisted hopping-type mechanisms of electron transport have been assessed for such systems with quantification of reorganization energies and comparisons between aqueous and RTIL electrolytes.[10, 20, 43-44] Ionic liquids have also proved to be very effective media for gating, with the totality of the electrode potential being experienced at the redox center with a viologen molecular bridge.

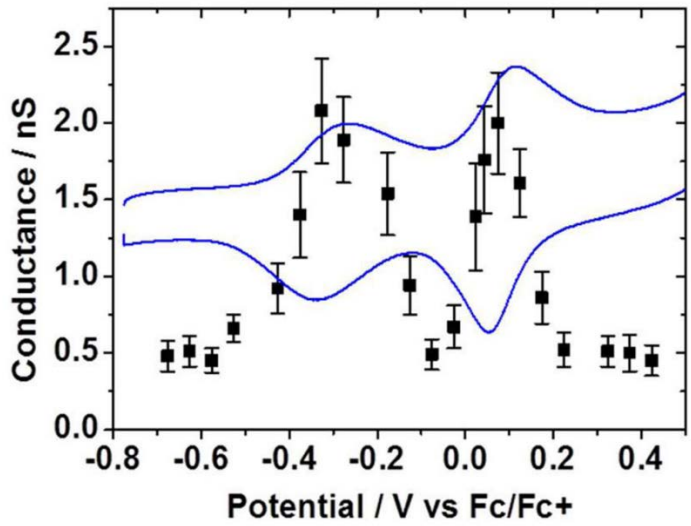

Figure 3. Single molecule conductance data for a pyrrolo-TTF molecular bridge with gold contacts plotted as a function of electrolyte potential. Data recorded in ionic liquid electrolyte. The blue solid curve is a superimposed CV for a self-assembled monolayer of the p-TTF compound on Au(111); the maxima in the single molecule junction conductance occur at the redox switching potentials. Reprinted with permission from reference [20]. Copyright 2012 American Chemical Society.

5.0 Beyond Gold Contacts

The overwhelming majority of single molecule electrolyte gating studies have employed gold contacts (i.e. gold substrates and STM tips). The reasons for this is that gold is oxide free in a wide double layer region, it has well-defined surface electrochemistry and there is a good choice of well-behaved anchoring groups, such as thiols and pyridyl. However, there are good reasons to develop other contacts, to explore, for example, how differences in the surface electronic structure and density of electronic states and surface electrochemical properties influence charge transport. Magnetic metal contacts also open up the possibility to study spin dependent transport and spintronics. In this respect, Brooke et al. have shown single molecule data recorded with nickel substrates and nickel tips for the bipyridine system, as shown in Figure 4.[45] Oxide free nickel surfaces were achieved by careful preparation and appropriate control of the electrode potential and choice of electrolytes. Here the single molecule conductance is shown as a function of the electrode potential and gating occurs even away from oxidation and reduction potentials. It is notable here that the conductance is higher with nickel contacts as compared to gold and also the conductance change with electrode potential (the electrochemical gating) is higher with nickel. These data could be rationalized by ab-initio calculations which took account of the spin-polarized Ni d-electrons and their strong spin hybridization with molecular orbitals of the bipyridine bridge to form a "spinterface".[45]

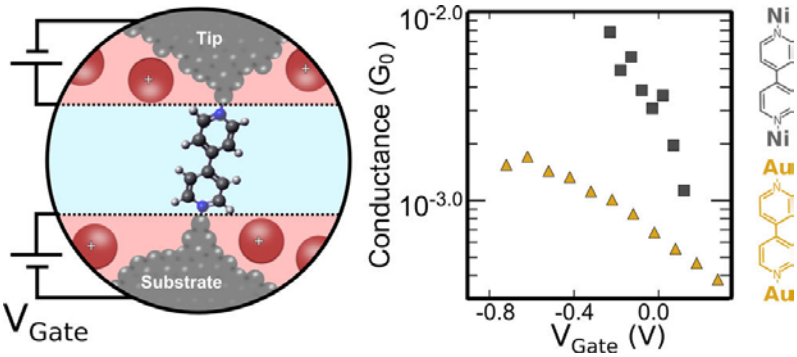

Figure 4 Left: an illustration of bipyridine bound between two oxide-free nickel contacts under electrochemical control. Right: Single molecule conductance versus electrode potential with gold and nickel contacts, respectively. Reprinted with permission from [45].Copyright 2015 American Chemical Society.

Very recently single molecule electrical measurements have been demonstrated with semiconducting substrates.[46-47] Although these measurements were recorded in the absence of electrochemical control, i.e. with just two electrodes, they give perspective for the future integration of semiconducting electrochemistry with single molecule electronics, to promote understanding of charge transfer to molecules at

semiconductor|electrolyte interfaces. Such studies could also help in gleaning details of the effect of electrode potential on surface state energetics and band alignment.

6.0 Further Technique Advancement

Single molecule electronics has been a highly active research field in the last 15 years and has greatly promoted the subject of molecular electronics and also analysis of charge transport in general. During this time there have been many important technical developments that have included advances in data analysis and measurement of other junction properties such as thermopower. Some of the technical advances made have as yet only be applied in 2-terminal configurations rather than in the bipotentiostatic configuration needed for electrochemical studies. Application of such new techniques could have a significant impact in electrochemical single molecule science. A particularly exciting development in this respect is the application of AC tip bias modulation methods to single molecule electrical junctions, however so far this has only been applied in the 2-terminal (non-electrochemical) setup.[48-49] This offers an exciting future outlook for electrochemical single molecule measurements given the importance of AC methods in electrochemistry in general. Perspectives here would be the analysis of molecular junction dynamics, determination of the AC response of redox active molecular junctions under electrochemical control and investigations of charge transfer in single molecule junctions with semiconductor contacts. In addition, following recent advances in technique development it is now also timely that external stimuli such as light and magnetic field are seamlessly integrated into the STM platform alongside electrochemical potential control. These offer light-activated collective oscillation of electrons and also their spin polarizations in these nanoscale junctions which enables new control and understanding of electron conduction and electron transfer in such single molecule junctions.

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